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Hollow fiber-based liquid–liquid–liquid micro-extraction with osmosis: I. Theoretical simulation and verification

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ABSTRACT

Osmosis in hollow fiber-based liquid–liquid–liquid micro-extraction (HF-LLLME) was validated and utilized to improve enrichment factor of extraction in this study. When donor phase (sample solution) with higher ion strength than acceptor phase (extraction phase) was used, osmosis was established from acceptor phase, through organic membrane to donor phase. The mass flux expression of analytes across the organic membrane was established based on the convective-diffusive kinetic model, and the kinetic process for HF-LLLME with osmosis was simulated. Simulation results indicated that osmosis from acceptor phase to donor phase can increase enrichment factor of HF-LLLME, accelerate extraction process, and even result in the distribution ratio of analytes between donor and acceptor phase exceeding their partition coefficient. This phenomenon was verified by the experimental data of extraction with six organic acids and four organic bases as the model analytes.

1. Introduction

Liquid–liquid extraction (LLE) is a conventional separation technique, and has been widely used [1,2] in sample preparation. However, for trace analysis, sample preparation method with higher enrichment factor and lower solvent consumption is required. In 1996, Jeannot and Cantwell [3] miniaturized LLE into liquid phase micro-extraction (LPME) and developed single drop LPME, in which a higher enrichment factor was obtained due to a larger volume ratio of the aqueous phase to the organic phase. In order to improve the stability and reliability of single drop liquid phase micro-extraction, Pedersen-Bjergaard and Rasmussen [4,5] introduced hollow fiber based LPME and developed its three-phase mode, hollow fiber based liquid–liquid–liquid micro-extraction (HF-LLLME), for the first time in 1999, which was used to extract ionizable and chargeable compounds from aqueous samples.

From then on, this method has been widely used in the analysis of environmental sample [6–10] and biological sample [11–13] due to its excellent enrichment factor and strong cleanup capability. In recent years, HF-LLLME has been largely improved by making some modifications all along. For example, Lee and co-worker [14] added salt into the donor phase in hollow fiber based LPME to improve the extraction efficiency by salting-out effect, which has been a common practice in HF-LLLME nowadays [15–17]. Rasmussen and co-workers [18] developed carrier-mediated HF-LLLME to promote the extraction of polar analytes. Jiang and and co-workers [19] used ionic liquid as supported liquid membrane to achieve high affinity to polar compounds. Other than these, binary solvent mixtures have been used as organic phase to increase extraction recoveries as compared to traditional unitary solvents [20]. The above-mentioned modifications all focused on the improvement of the partition coefficient of analytes to increase the extraction efficiency and selectivity. Recently, other methods have been developed to facilitate the kinetic mass transfer of analytes [9], including dynamic HF-LLLME [21], HF-LLLME under sonication [22], HF-LLLME with nano-magnetic powder [23], and so on. Among these methods, dynamic HF-LLLME showed relatively higher enhancement factor, and has been studied further [24,25]. However, as regular micro-extraction methods, HF-LLLME still suffers from the common drawback of low recovery of analytes, and there is no essential solution until recently [9].

Osmosis is a ubiquitous phenomenon that water or other solvents can automatically flow across semi-permeable membranes when an osmotic pressure difference exists between two sides of the membrane [26,27]. A lot of membranes can act as semi-permeable membranes for water if they can exclude the ions but admit the transfer of water [28], such as reverse osmosis (RO) membrane (cellulose acetate membrane, aromatic polyamide membrane, etc.) [29], plant plasma membrane [30], and clays [28]. Osmosis is widely utilized for water purification, desalination in chemical industry [27,29], but rarely employed in chemical analysis.

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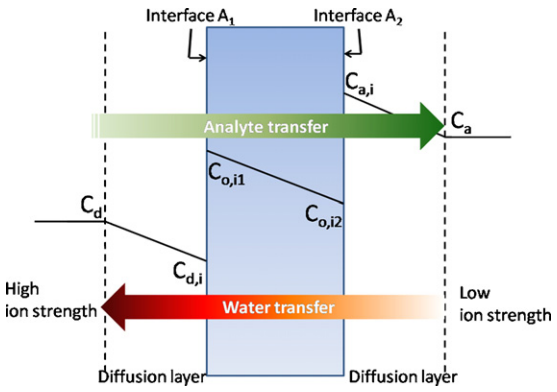

Fig. 1. Schematic mass transferring process in HF-LLLME with osmosis. C_d, C_o and C_a are the analytes concentrations in donor phase, organic (intermediate) phase and acceptor phase, respectively. The subscript i refers to concentrations immediately adjacent to the interface.

In present work, osmosis through hollow fiber supported organic membrane was observed in HF-LLLME experiments when a large amount of salt was added into the donor phase, and the benefits of osmosis to HF-LLLME have been proven. To investigate the effect of osmosis on the extraction, the mass flux expression of analytes across the membrane was established based on the fundamental theory of mass transfer kinetics in liquid phase microextraction [3], and the kinetic process for HF-LLLME with osmosis had been simulated by integrating the flux expression. The integration result showed that osmosis during HF-LLLME can cause dynamic concentration of analytes in the acceptor phase due to the reduction of acceptor phase volume during extraction. Thus, it can increase enrichment factor of HF-LLLME, accelerate extraction process, and even make the distribution ratios of analytes between donor and acceptor phase exceed their partition coefficients. Furthermore, the mass transfer simulation of HF-LLLME was verified by the experimental data of six common organic acids and four organic bases that were used as model analytes, and the breakthrough to the equilibrium of the system was observed clearly by comparing the distribution ratio of analytes during extraction time with the partition coefficient of analytes.

2. Theory

2.1. Mass transfer of analytes in HF-LLLME process

Based on convective-diffusive kinetic model which had been used earlier for mass transfer kinetics study of two phases microextraction [3], the transfer steps of HF-LLLME can be illustrated as Fig. 1. A porous membrane supported liquid membrane acts as the organic phase between donor (sample) phase and acceptor (extraction) phase. Boundary layer is assumed to present on the membrane surface adjacent to donor phase. Analytes transfer steps include diffusion under a concentration gradient across the boundary layer, partitioning of the analyte in the membrane, diffusion under a concentration gradient across membrane, and finally partitioning into the acceptor phase.

The general analyte flux for HF-LLLME can be written as

$$\frac{dn_a}{dt} = A_2\overline{\beta}\left(K_{a/d}\left(\frac{C_{d,initial}V_d - C_aV_a}{V_d}\right) - C_a\right) \quad (1)$$

where n_a is the mass of analyte in the acceptor phase at time t, A_2 is the interfacial area between organic phase and acceptor phase, $\overline{\beta}$ is the overall mass transfer coefficient with respect to the acceptor phase (in cm/s), $C_{d,initial}$ is the initial analyte concentration in the donor phase, V_d is the volume of donor phase, C_a is the analyte concentration in the acceptor phase at time t, V_a is the volume of acceptor phase, and $K_{a/d}$ is the distribution ratio of analytes between acceptor phase and donor phase at equilibrium (acceptor/donor partition coefficient).

Eq. (1) is deduced as follows:

Analyte flux at two interfaces can be expressed as:

$$\frac{dn_1}{dt} = A_1\beta_d(C_d - C_{d,i}) = A_1\beta_o(C_{o,i1} - C_{o,i2}) \quad (2)$$

$$\frac{dn_2}{dt} = A_2\beta_a(C_{a,i} - C_a) = A_2\beta_o(C_{o,i1} - C_{o,i2}) \quad (3)$$

Assuming that the distribution of analytes across the liquid–liquid interface is instant, and equilibrium is reached at the interface at all times, so

$$K_{o/d} = \frac{C_{o,i1}}{C_{d,i}} \quad (4)$$

$$K_{a/o} = \frac{C_{a,i}}{C_{o,i2}} \quad (5)$$

where C_o is the analyte concentration in the organic phase (membrane) at time t, while the subscript i refers to concentrations immediately adjacent to the interface. 1 and 2 refer to the outer side and inner side of hollow fiber, respectively. β_a, β_d, β_o are the individual mass transfer coefficients of analytes in the acceptor phase, donor phase and organic phase, respectively.

After substitution from Eqs. (2), (4) and (5), Eq. (3) can be written as

$$\frac{dn_a}{dt} = A_2\overline{\beta}(K_{a/d}C_d - C_a) \quad (6)$$

where $\overline{\beta}$ is expressed as

$$\frac{1}{\overline{\beta}} = \frac{1}{\beta_a} + \frac{K_{o/d}}{\beta_o} + \frac{K_{a/d}}{\beta_d} \quad (7)$$

If $C_{o,i1}$ and $C_{o,i2}$ are always smaller than C_a, and volume of organic phase (V_o) is much smaller than V_a, C_d can be simply expressed as

$$C_d = \frac{C_{d,initial}V_d - C_aV_a}{V_d} \quad (8)$$

Eq. (1) is obtained by substituting Eq. (8) for C_d in Eq. (6).

Eq. (1) can be integrated as follows when all the parameters keep constant with time:

$$n = n_{a,eq} - n_{a,eq}e^{-kt} \quad (9)$$

in which, $n_{a,eq}$ represents the analyte mass in acceptor phase at the equilibrium, and

$$k = A_2\bar{\beta}\left(\frac{K_{a/d}V_a + V_d}{V_dV_a}\right) \quad (10)$$

2.2. Mass transfer of analytes in HF-LLLME with osmosis

When osmosis occurs, water would transfer from the acceptor phase to donor phase through organic phase during extraction. Thus, V_a and A_2 is the function of time expressed as $f_1(t)$ and $f_2(t)$, then Eq. (1) can be modified as

$$\frac{dn}{dt} = f_2(t)\overline{\beta}\left(K_{a/d}\left(\frac{C_{d,initial}V_d - n}{V_d}\right) - \frac{n}{f_1(t)}\right) \quad (11)$$

Assuming that the change of osmotic pressure $\Delta\pi$ during extraction can be neglected, and the trans-membrane pressure Δp is much smaller than $\Delta\pi$, the water flux during extraction is constant [27]. Thus, $f_1(t)$ and $f_2(t)$ are linear functions of time, and can be expressed as

$$V_a = f_1(t) = V_{a,0} - N_At \quad (12)$$